COMPOSITIONS AND METHODS FOR CONTROLLING THE RELEASE OF CHEMICALS PLACED ON PARTICULATES

Background of the Invention

1. Field of the Invention

[001] The present invention relates to methods and compositions for treating subterranean formations, and more specifically, to improved methods for creating and using particulate materials having treating agents absorbed thereon and coated with a degradable coating material.

2. Description of the Prior Art

[002] Particulate materials are often introduced into subterranean zones in conjunction with fracturing and sand control treatments.

[003] A subterranean formation may be treated to increase its conductivity by hydraulically fracturing the formation to create one or more cracks or "fractures." Such hydraulic fracturing is usually accomplished by injecting a viscous fracturing fluid into a subterranean formation at a rate and pressure sufficient to cause the formation to break down and produce one or more fractures. The fracture or fractures may be horizontal or vertical, with the latter usually predominating, and with the tendency toward vertical fractures increasing with the depth of the formation being fractured. The fracturing fluid is generally a gel, emulsion, or foam that may comprise a particulate material often referred to as a proppant. When used, the proppant is deposited in the fracture to prevent the fracture from fully closing and to maintain conductive channels through which produced fluids can flow upon completion of the fracturing treatment and release of the attendant hydraulic pressure.

[004] Sand control treatments may be used to reduce the migration of unconsolidated formation particulates into the wellbore. One such sand control treatment involves the use of a "gravel pack." One common type of gravel packing operation involves placing a gravel pack screen in the well bore and packing the surrounding annulus between the screen and the well bore with gravel of a specific size designed to prevent the passage of formation sand. The gravel pack screen is generally a filter assembly used to retain the gravel placed during gravel pack operation. A wide range of sizes and screen configurations are available to suit the

characteristics of the gravel used. Similarly, a wide range of sizes of gravel is available to suit the characteristics of the unconsolidated or poorly consolidated particulates in the subterranean formation. The resulting structure presents a barrier to migrating sand from the formation while still permitting fluid flow. When installing the gravel pack, the gravel is carried to the formation in the form of a slurry by mixing the gravel with a transport fluid. Gravel packs act, *inter alia*, to stabilize the formation while causing minimal impairment to well productivity. The gravel, *inter alia*, acts to prevent the particulates from occluding the screen or migrating with the produced fluids, and the screen, *inter alia*, acts to prevent the gravel from entering the production tubing.

[005] In addition to being useful in fracturing and sand control operations, particulates also may be used to carry a variety of treating agents that may be useful in the subterranean zone. Treating agents may be placed onto particulate material by, for example, impregnation, deposition, or adsorption thereon. Examples of such treating agents include, but are not limited to, gel breakers, scale inhibitors, biocides, corrosion inhibitors, paraffin inhibitors, and other any other treating agent that does not adversely impact the formation or the proppant pack. However, treating agents placed on particulate material and introduced into a subterranean zone often dissolve into the fluids present in the subterranean zone too rapidly. When the treating agents dissolve too rapidly, they may not remain in the subterranean formation for a long enough period of time or may not be delivered to the desired location in the subterranean formation. High sheer rates in the subterranean zone, high temperature, and solubility and interaction with delivery and formation fluids are factors known to increase the rate at which the treating agents dissolve off of the particulate material.

SUMMARY OF THE INVENTION

[006] The present invention relates to methods and compositions for treating subterranean formations, and more specifically, to improved methods for creating and using particulate materials having treating agents absorbed thereon and coated with a degradable coating material.

[007] One embodiment of a method of the present invention provides a method of treating to a subterranean formation comprising placing a coated, treated particulate into a subterranean formation wherein the coated, treated particulate comprises a particulate material having a treating agent placed thereon and a substantially complete layer of a degradable coating material placed thereon over the treating agent.

[008] Another embodiment of the present invention provides a chemically treated, coated particulate material comprising a particulate material having a treating agent placed thereon and a substantially complete layer of a degradable coating material coated placed thereon over the treating agent.

[009] The objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments which follows.

DESCRIPTION OF PREFERRED EMBODIMENTS

[010] The present invention relates to methods and compositions for treating subterranean formations, and more specifically, to improved methods for creating and using particulate materials having treating agents absorbed thereon and coated with a degradable coating material.

[011] In the methods and compositions of the present invention, treating agents are adsorbed onto a particulate material, such as proppant or gravel, for introduction into a subterranean formation. In certain embodiments of the present invention, once the treating agents are adsorbed onto a particulate material, the particulate material is coated with a degradable coating material that temporarily shields the chemical from the fluids present in the subterranean formation until at least a portion of the coating degrades away, at which point the treating agent is exposed to the fluids in the subterranean formation and begins to be released. When a coated and treated particulate is mixed with a liquid such as a servicing fluid, the treating agent is gradually released into the servicing fluid as the degradable coating gradually degrades or dissolves.

[012] Any particulate material suitable for use in conjunction with subterranean applications is suitable for use as the particulate material in the compositions and methods of the present invention. For instance, natural sand, quartz sand, garnet, glass, walnut hulls, nylon pellets, bauxite, ceramics, polymeric materials, carbon composites, natural or synthetic polymers, resin beads, and mixtures thereof are suitable. Suitable sizes range from 4 to 100 U.S. mesh, in certain preferred embodiments the sizes range from 10 to 60 US mesh. The proppant particles may be in any form, including that of regular or irregular pellets, fibers, flakes, ribbons, beads, shavings, platelets and the like. In some embodiments of the present invention, it is preferable for the particulate material to exhibit a surface geometry such that at least one recessed or depressed area exists along the surface of the particulate. Such a particulate surface geometry is referred to herein as porous, or partially hollow.

[013] The methods of the present invention can be used to deliver almost any treating agent, including but not limited to gel breakers, acids, oxidizers, enzymes, hydrolyzable esters, scale inhibitors, biocides, corrosion inhibitors, paraffin inhibitors, cement slurry set accelerators, cement slurry set retarders, cement slurry dispersants, cement slurry fluid loss control additives, cement slurry thixotropic additives, cement slurry suspending agents, or substantially any other

chemical that is soluble in the formation fluids under the environmental conditions of the formation within which it is placed. The degradable coating material of the present invention protects the treating agent from exposure to the formation fluids and environmental conditions until that degradable coating degrades away. As the degradable coating is lost, the treating agent is slowly released by contact with the fluids in the subterranean formation.

[014] The treating agent may be impregnated, deposited, coated, permeated, or saturated onto the particulate material. For the purposes of this application, the term "adsorbed" will be used to refer to any method known in the art to incorporate a chemical with a solid particulate. Any such method known in the art that allows a treating agent to be physically incorporated with a particulate material in a manner in which it is later able to leech off of the particulate material is suitable for use in the present invention. In one method of placing a desired treating agent onto a particulate known in the art, a liquid treating agent is adsorbed onto a particulate material by simply spraying the treating agent onto the particulate material in an amount such that the particulate material surface is substantially dry after the adsorption is substantially complete. Another method involves mixing the treating agent with a solvent, adsorbing the solvent/agent mixture onto the particulate material, and then allowing the solvent to substantially evaporate from the surface of the particulate over time or under vacuum conditions. This method may be used where the treating agent is solid at room temperature to facilitate the coating process. One skilled in the art, with the benefit of this disclosure, will be able to determine the proper amount of chemical to place onto the particulate and a method for placing the desired treating agent onto the particulate. In some embodiments, the amount of treating agent absorbed onto the particulate material ranged from about 0.1% to about 50% by weight of the particulate material. In other embodiments, the amounts of treating agent adsorbed onto the particulate can be several times the weight of the particulate depending on the agent chosen and the desired effect.

[015] By adsorbing the treating agent on the particulate material as in the methods of the present invention, the treating agents are not subject to the gravity segregation or premature settling out of the servicing fluid that carries the agent into the subterranean formation. This allows the treating agent to be substantially uniformly dispersed along with the particulate material without undesired segregation or settling, and enables uniform release of the treating agent within the formation.

[016] The degradable coating materials suitable for use in the present invention are those compounds that degrade over time in the subterranean formation. Any material capable of acting as a temporary barrier between the fluids in the subterranean formation and the chemical carried on the particulate material and that does not undesirably interfere with the subterranean formation, the particulate, or the treating agent is suitable for use as a coating material in the present invention. It is not necessary for the degradable coating material to cover 100% of the surface area of the impregnated particulate. Rather, the degradable coating material need only cover enough of the particulate's surface area to delay the release of the adsorbed treating agent in the formation to a desired extent. In one embodiment of the present invention, the surface area is coated to a sufficient extent as to allow the particulates to be placed in a desirable location in the subterranean formation before the majority of the treating agent is released.

[017] Degradable materials that may be used in conjunction with the present invention are those materials than can be coated onto a particulate and, in preferred embodiments, are substantially water insoluble such that they degrade over time, rather than instantaneously. Examples of suitable degradable materials include substantially water insoluble esters such as ortho esters; poly(orthoesters); aliphatic polyesters; lactides, poly(lactides); glycolides; poly(glycolides); poly(ε-caprolactone); poly(hydroxybutyrate); substantially water insoluble anhydrides; poly(anhydrides); and poly(amino acids).

[018] Polymers suitable for use as a degradable material of the present invention may be considered degradable if the degradation is due, *inter alia*, to chemical and/or radical process such as hydrolysis, oxidation, or enzymatic decomposition. The degradability of a polymer depends at least in part on its backbone structure, type of repetitive unit, composition, sequence, length, molecular geometry, molecular weight, morphology (*e.g.*, crystallinity, size of spherulites, and orientation), hydrophilicity, hydrophobicity, surface area, and additives. Also, the environment to which the polymer is subjected may affect how it degrades, *e.g.*, temperature, presence of moisture, oxygen, microorganisms, enzymes, pH, and the like.

[019] Blends of certain degradable materials may also be suitable as the degradable coating materials of the present invention. One example of a suitable blend of materials is a mixture of poly(lactic acid) and a poly(anhydride) where the mixing of an acid and base could result in a neutral solution where this is desirable. Another example would include a blend of poly(lactic acid) and boric oxide. Other materials that undergo an irreversible degradation may

also be suitable, if the products of the degradation do not undesirably interfere with either the conductivity of the proppant matrix or with the production of any of the fluids from the subterranean formation.

[020] In choosing the appropriate degradable material, one should consider the degradation products that will result. The degradation products should not adversely affect other operations or components. The choice of degradable material also can depend, at least in part, on the conditions of the well, *e.g.*, wellbore temperature. For instance, lactides have been found to be suitable for lower temperature wells, including those within the range of 60°F to 150°F, and polylactides have been found to be suitable for well bore temperatures above this range.

[021] A preferable result is achieved if the degradable material degrades slowly over time as opposed to instantaneously. Even more preferable results have been obtained when the degradable material does not substantially degrade until after the particulate impregnated with a treating agent has been placed in a desired location in the subterranean formation. Even more preferable results have been obtained when the coating material does not substantially degrade until after the operation delivering the particulate, such as a fracturing operation or gravel packing operation, is substantially complete.

[022] Where the chosen degradable coating material is a solid material at ambient temperatures it may be advantageous to mix it with a solvent to facilitate the coating of the degradable coating material onto the particulate material. A variety of solvents known in the art are suitable for this purpose in the present invention. Some suitable solvents include, but are not limited to acetone, propylene carbonate, dipropylene glycol methyl ether, methylene chloride, isopropyl alcohol, and combinations thereof.

[023] In some embodiments of the present invention the particle material is coated with from about 0.1% to about 30% degradable coating material by weight of the particulate material. In some embodiments of the present invention, all of the treated particle material used in the subterranean operation is coated with a degradable coating material while in other embodiments, only a portion of the particulate material is coated. It is within the ability of one skilled in the art, with the benefit of this disclosure, to determine the thickness of degradable coating that should be applied to the treated particulate material and the percentage of the treated particulate material that should be coated.

[024] In one embodiment of a method of the present invention, a treating agent is absorbed onto a particulate material after which the absorbed particulate material is coated with a degradable coating material and the absorbed, coated particulate material is placed into a subterranean formation. Once in the formation, the coating material degrades off of the particulate material, exposing the treating agent, which is then released into the subterranean formation.

[025] Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit and scope of this invention as defined by the appended claims.